

SCIENCE FOR CERAMIC PRODUCTION

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CHARACTERISTICS OF HIGH-DENSITY TECHNICAL CERAMICS TECHNOLOGY. STRUCTURE REGULATION DURING SINTERING

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The sintering characteristics of oxide powders with different dispersity are examined. Powders with nanosize particles sinter by the diffusion-viscous flow mechanism. This makes it possible to obtain dense and strong materials in different media.

To obtain dense oxide ceramic materials from highly dispersed powders the goal is almost always to achieve the highest possible density. High sintering temperatures and prolonged holding are recommended. However, it is known that such conditions result, in most cases, in intense growth of crystals and slower removal of closed porosity, which forms at the final stage of sintering. In practice, oxide ceramic materials with the main oxide content of about 99.9% are characterized by comparatively low properties and a microstructure that is difficult to regulate, and in ordinary solid-phase sintering the density never comes close the theoretical value. The properties of the ceramic depend on the characteristics of the commercial powders used and the heating regime (temperature, sintering time, gas medium). Certain data on the degree of sintering, microstructure, and strength of the number of pure oxide materials are presented in Table 1.

The data presented show that ceramic made from pure oxides can be used, apparently, only in cases where high mechanical characteristics are not required (surface cleanliness, impact resistance, heat resistance, and so forth), i.e., only as an electric insulator, high-temperature and chemically resistant material.

Investigations where a change of microstructure and properties as a result of sintering and thermal “aging” were examined have made it possible to study porosity removal processes and determine the desirability of prolonged heat-

ing to achieve maximum density. These investigations were performed for aluminum, magnesium, calcium, yttrium, and scandium oxides as well as alumomagnesia spinel and yttrium zirconate. It was determined that all materials show a gradual increase of density under prolonged heating, but the degree of compaction does not reach 100%. Pore removal slows down markedly when growing crystals trap pores. The oxide vapor pressure becomes important, since open porosity forms under intense evaporation.

Experiments have shown that the relative density of materials does not exceed 98% of the theoretical value with prolonged isothermal heating. As a rule, the materials possess a coarse-crystal structure with low strength. Therefore, high temperatures and long holding times when sintering pure oxides cannot give the maximum density and optimal properties. It can be said with great confidence that sintering of pure oxides under such conditions is undesirable. Consequently, it is better to change the activity of powders, which makes it possible in a number of cases to obtain ceramic density above 98–99% of the theoretical value.

The rate and degree of sintering of oxide materials are determined by the dispersity of the initial particles, even-grained texture, and the defect density of the crystal lattice. In practice, to obtain sufficiently high dispersity of oxides, for example, aluminum or zirconium oxide, prolonged wet milling is ordinarily used (often for several tens of hours), giving powders with 1–3 μm particles. Using a different method, where the goal is to increase the activity of powders with respect to sintering, the powders are obtained by heating compounds of elements at comparatively low temperatures; special methods are also used. For example, MgO powders,

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TABLE 1.

Material	Sintering temperature, °C	Relative density, %	Crystal size, μm	Bending strength, MPa
Al_2O_3	1720	96.5	30 – 40	140 – 150
MgO	1700	97.0	30 – 50	100 – 120
BeO	1720	95.5	35 – 50	120 – 140
CaO	1900	94.0	50 – 60	100
Y_2O_3	2000	96.0	60	100 – 120
Sc_2O_3	2000	95.5	10 – 12	120 – 180
$\text{MgO} \cdot \text{Al}_2\text{O}_3$	1710	95.5	10 – 15	135 – 150
$3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$	1780	97.5	150 – 100	130 – 150
ZrO_2 (stab.)	1750	96.5	40 – 50	180 – 200

obtained from magnesium hydrocarbonate, as well as aluminum oxide powders, obtained by heating aluminosilicates, sinter quite adequately. However, this cannot be achieved for all compounds. In many cases, the powders having a high specific surface area are not distinguished by high sintering rates because of particle aggregation, which impedes active removal of pores. It is due either to inheritance of structure, when the aggregate structure of the particles of an intermediate compound is transferred to oxide powder particles, or very high defect density in the particles, which causes the particles to sinter even as the compounds are being obtained. Therefore, often, the specific surface area cannot be used to characterize the sintering activity of a powder. Since the aggregated powders ordinarily have an extended surface area of the particles comprising the aggregates, their degree of sintering is low.

The influence of the temperature of deposition of yttrium oxalate on the dispersity and sintering of yttrium oxide powders obtained by heating at 800°C has been studied from the positions examined here. The deposition was performed under industrial conditions from a dilute chloride solution with molar content 0.02% and solution temperature 20, 50, and 80°C. The powders obtained differ substantially with respect to dispersity and structure: the content of aggregates less than 3 μm in size was 89, 34, and 1.0%, respectively. Samples were pressed under pressure 100 MPa and then vacuum sintered at 1750°C with a holding time of 2 h. The properties of the powders, compacts, and sintered samples of Y_2O_3 are presented in Table 2.

Only samples fabricated from powder with the largest specific surface area and smallest aggregates showed satisfactory sintering. The powder was obtained from oxalate at solution precipitation temperature 20°C. This behavior is due to a difference in the structure and size of the aggregates, inherited from the structure of the initial oxalates; this was also observed for other materials.

It should be noted that all conventional methods which can be used to increase the rate of sintering do not solve the main problem — increasing the density of ceramic up to

TABLE 2.

Indicator	Properties at oxalate deposition temperature, °C		
	20	50	80
Specific surface area of the powders, m^2/g	45.0	16.0	1.6
Content of aggregates, %:			
< 6 μm	97	60	3
< 3 μm	89	34	1
Relative density of, %:			
compacts	41.7	47.3	55.3
sintered samples	96.2	92.2	78.0
Lineal shrinkage accompanying sintering, %	25.2	17.7	9.4

complete removal of the porosity. In all cases only the sintering temperature decreases; the relative density is 96 – 98% of the theoretical value. In principle, the relative density can be increased to 99% and even materials showing some light transmission can be obtained, but closed porosity always remains inside crystals and cannot be removed.

The density of ceramic oxide materials can be increased during sintering only by limiting the growth of crystals, slowing down the sintering enough to ensure pore removal before this process begins. This can be done only by introducing additives. Additives also impart special prescribed properties to ceramic materials (density close to the theoretical value, transparency, fine-crystalline structure, high strength, heat resistance, and so forth). The effect of an additive is determined by the chemical nature, concentration, and degree of uniformity of its distribution in the particles of the main oxide powder.

A very effective method for increasing the density of oxide ceramic and for regulating the microstructure and properties is to introduce additives which form solid solutions. In this way it is possible to vary the porosity of a ceramic and the degree of the crystallization over wide limits. For example, additives forming solid heterovalent substitution solutions make it possible to obtain density close to the theoretical value.

The effectiveness of the presence of any heterovalent ion can be seen for the example of HfO_2 introduced into yttrium oxide to obtain optically transparent ceramic. Moreover, it is convenient to study the influence of the dispersity of the initial particles on such materials, since transparency is a convenient property for characterizing the quality of the materials used. Just as in the preceding case (see Table 2), oxalates were precipitated from a mixture of chloride solutions of oxalic acid whose temperatures are 20, 50, and 80°C. The precipitated powders still remain strongly aggregated even at solution temperature 20°C. A ceramic obtained from powders which in turn were obtained by heating the initial oxalates without preliminary comminution are characterized by

TABLE 3.

Indicator	Properties at the oxalate precipitation temperature, °C		
	20	50	80
Powders:			
specific surface area of aggregates, m ² /g	21.0	6.5	3.0
size of aggregates in oxalate powders, μm	10 – 12	15 – 20	20 – 30
size of comminuted aggregates* after heating at 1000°C, μm	2	4	5
Ceramic:**			
apparent density, g/cm ³	5.17	5.15	5.14
light transmission (wavelength 0.7 μm, sample thickness 1.5 mm), %	70	62	50

* Milling time 15 h.

** Samples compacted at pressure 100 MPa, sintering in vacuum at 2000°C with holding time 3 h.

very low optical parameters, since in this case the presence of aggregates does not permit sintering samples to the theoretical density. Disaggregation of the oxalates was performed in a ball mill by the wet method, after which the oxalates were heated to temperatures 1000 and 1400°C. The sizes of the aggregates are essentially independent of the heating temperature; they are determined by the precipitation temperature of the oxalates and the milling time.

The powders of the solid solutions obtained by heating at 1000°C oxalates precipitated at 20°C and ground for 15 h in a ball mill consisted of 1 – 2 μm particles. The particles of oxalates precipitated at 80°C were 3 – 5 μm in size, and these powders were more aggregated. The properties of powders and ceramic with the composition 0.94Y₂O₃ – 0.06HfO₂ are presented in Table 3. The aggregates of powder obtained by heating oxalates at 1400°C are only somewhat larger; substantial recrystallization is not observed in them.

This example shows that the additive sharply increases the density of the material. Complete pore removal is achieved

right up to a transparent state. At the same time, light transmission depends strongly on the choice of technological methods and regimes used for powder preparation.

It is evident at the same time that, up to now, answers to the questions of which additive should be introduced and in which cases and in what amount it should be introduced to obtain the desired effect are largely obtained experimentally in most cases. The difficulties of generalizing the experimental data are due to the diversity of the phenomena due to the additives. They can change the concentration of point and extended defects and thereby the diffusion mobility of the elements of the crystal lattice and properties which depend on it. Specifically, focusing on dislocations, impurity atoms change the mobility and thereby influence the rate of processes. Remaining undissolved, inclusions of a second phase can hinder the diffusion of atoms from small crystals to large crystals, limiting recrystallization. The relative fraction of these phenomena depends on the character of the interaction of the additive with the main oxide. The degree of sintering, the microstructure, and the properties of oxide materials can be regulated over wide limits by varying the nature of the additive.

Combined additives, forming solid isovalent and heterovalent substitution solutions simultaneously, are very effective in acting on sintering, microstructure, and strength. An example is Y₂O₃ – Sc₂O₃ – HfO₂ ceramic, whose compositions and properties are presented in Table 4.

In many cases the effectiveness of additives is seen only when sintering is conducted in a definite gas medium, i.e., when there are no factors which impede pore removal. Such media are usually vacuum, hydrogen, or oxygen. A comparison of the behavior of yttrium oxide ceramic with zirconium dioxide additive in air and vacuum can serve as a manifestation of the effective simultaneous action of an additive and the gas medium. In air, the material after being heat-treated at 1700°C possesses porosity 35 – 40%, whereas in vacuum at the same temperature it becomes transparent, i.e., it acquires the theoretical density. Such a sharp difference in sintering between vacuum and air is due to the intensity of diffusion in solid solutions in media with different oxygen partial pressure.

TABLE 4.

Ceramic composition*	Light transmission,** %	Average crystal size, μm	Crystal microhardness, MPa	Lattice parameter of solid solution, nm	Bending strength, MPa
0.77Y ₂ O ₃ – 0.2Se ₂ O ₃ – 0.03HfO ₂	80	8 – 10	12,500	1.0217	250
0.67Y ₂ O ₃ – 0.3Se ₂ O ₃ – 0.03HfO ₂	79	7 – 8	13,700	1.0195	280
0.75Y ₂ O ₃ – 0.2Se ₂ O ₃ – 0.05HfO ₂	78	10 – 12	15,000	1.0182	220
0.65Y ₂ O ₃ – 0.3Se ₂ O ₃ – 0.05HfO ₂	75	20 – 25	14,000	1.0205	200

* Vacuum sintering temperature 1800°C.

** Wavelength 0.7 μm, sample height 4 mm.

Thus, it is evident that many factors, which determine pore removal and microstructure formation in a ceramic during sintering, must be used to obtain ceramic materials with prescribed properties. These include the characteristics of the initial powder and the sintering regime and gas medium.

The theoretical models proposed in [2] consider mainly the mechanisms of the increase in the contact radius between particles in model experiments; they are based on the idea of a single contact or single pore. Two fundamental assumption in these models is that the point where two particles touch remains stationary and that the shrinkage is a result of atomic transfer of material along the direction toward this point, which in time lies at the center of the contact neck. The characteristics observed during sintering of particles in real compacts are often substantially different from those established by using models.

Such ideas are mainly adequate for describing the behavior of comparatively rough powders obtained by mechanical comminution — milling. They often retain the crystal structure, although it is possible to achieve very high degrees of distortion of this structure right up to the formation of amorphous surface layers. Their dispersity is usually characterized as “of the order of a micron” — from several microns (as a rule, 3 – 5 μm) to several tenths of a micron (more than 0.3 – 0.5 μm). Such powders have high energy as a result of the presence of a highly extended surface with large local changes of the curvature.

Flows from extended to compressed zones (i.e., from concave to convex sections) arise at a contact between particles under the action of surface tension in individual sections of a porous body; atoms flow in the opposite direction. As a result of mass transfer, particle centers converge toward one another and pores grow, i.e., local deformation processes determined by diffusion flows occur. The rate of the process is determined by the effective diffusion coefficient, which depends on the concentration and mobility of vacancies. The concentration is established by their form — normal, nonstoichiometric, impurity; in addition, irrespective of their origin, they all participate together in the mass transfer. Experiments show that the number of vacancies can be most effectively regulated by introducing additives which enter the lattice in the form of a solid solution. Vacancy mobility is determined by the form of the path along which a vacancy emerges at the surface of the body, i.e., by the form of the lattice defect which facilitates the motion of the vacancy. The mobilities along surfaces (outer and inner), boundaries, and dislocations as well as through the volume (in the absence of defects) are distinguished.

Large particles become compacted, mainly by diffusion-viscous flow. Ordinarily, three stages of compaction are distinguished: initial, intermediate, and final [2]. Sintering of powder particles at the locations where they come into contact by means of diffusion along a surface occurs at the initial stage. The porous body that is formed deforms as a viscous medium at the intermediate stage, and mass transfer actually

occurs in layers near the surface. At the final stage the pores dissolve via vacancies in the crystal as result of volume diffusion; vacancies emerge onto intercrystalline boundaries and then at the surface. The inner surfaces — pores — can also be vacancy sinks and increase in volume (coalescence of pores). Crystal growth is observed at the final stage of compaction, when the porosity reaches 5 – 10%; during the preceding stages inclusions of pores slow down crystal growth. Large pores, formed as a result of coalescence, as well as pores trapped by a growing crystal actually do not close even with high sintering temperatures of the ceramic and prolonged holding periods. This is the main reason why ceramic obtained by conventional methods is of quite low quality.

The mechanism of particle deformation during compaction of highly dispersed and highly defective powders obtained by chemical methods is different from the mechanism presented above. The driving force is the same — surface tension, and the elementary processes are the same — diffusion-viscous flow. However, in addition to movement of atoms, adjustment occurs by means of shear, rotation, i.e., by restructuring of bonds in strongly deformed “x-ray amorphous” particles close to the surface state. The result of such processes is coalescence of particles, similar to merging, where embryos can reach large sizes. One can imagine that drops which have merged and grow in size will ultimately manifest the properties of crystals, i.e., there will arise in them definite directions and planes of growth, which in the general force field will not differ sharply from individual particles, since the field orients them. Correspondingly, large neighboring particles likewise will not be strongly disoriented, which allows crystals to grow by adjusting without mass transfer over appreciable distances. The force field generated by the general crystal lattice facilitates this. An analogy can be drawn between such processes and recrystallization. Indeed, the lattice perceives such inclusions as volume defects and strives to lower its energy by ordering the bonds between individual sections. It should be noted that this phenomenon can be observed only in sufficiently pure crystals of oxides, their compounds, or solid solutions, since segregation of impurities on boundaries impedes adjustment.

Thus, a highly dispersed blank is a highly porous medium with inclusions of small pores that deforms rapidly. This is determined by the high curvature of the surface of the particles, which is inversely proportional to the radius. The surface of the particles is very extended and subjected to large forces determined by surface tension and the specific surface area. All this is the reason for high local saturation of vacancies, which, in turn, possess high mobility along a surface. Most likely, such a body should be viewed as a single entity. To a first approximation, apparently, it is possible to use volume models of deformation, although all characteristics of vacancies (specifically, concentration and mobility) must be surface characteristics [3]. It is true that the qualitatively different state of the particles and the boundaries between them is not taken into account adequately in this case.

As a result, boundaries cannot attach during crystal growth from such small pores with large surface curvature.

A compact produced from highly dispersed powder, obtained by a chemical method in fast nonequilibrium processes, deforms during sintering as a single defective matrix, in which the state of the atoms is close to a surface state and the chemical bonds are only partially compensated. A dense grid of short boundaries between small particles does not permit crystal growth to develop, and pores are an effective obstacle to the motion of boundaries as a whole. Particles move by shear and rotation accompanying adjustment. The pores of the matrix do not close, but rather “float to the surface” (as in a liquid) by diffusion. Crystals grow when the porosity is low and the pores are small, smaller than the critical value. In other words, the pores close, as result of which a nonporous and transparent state of the ceramic is attained. Apparently, nanosize powders exhibit special behavior, and here one must talk about not atoms on a surface or the state of atoms on a surface but rather about the surface state of the substance. The state of highly dispersed powders is inherited by a fine-crystalline ceramic fabricated from them; the ceramic possesses a more open structure. This is seen as a decrease of its microhardness, refractive index, pycnometric density, and melting temperature [4].

In addition, the experimental data show that the use of additives which form solid solutions accelerates compaction to such an extent that pore removal precedes crystal growth, which starts only when essentially all pores are removed, i.e., these are separate processes. In this case, crystals grow without pores, making it possible to obtain transparent ceramic materials. The sintering in the case of aggregates of the ini-

tial powder a fraction of a micron in size occurs at the final stage by lattice adjustment near boundaries with deformation of the particles as a result of diffusion, whose rate is high due to the additive forming a solid solution.

The sintering activation energies determined for some of the materials investigated are 100 – 150 kJ/mole. This is approximately 2 – 3 times less than the sintering activation energy of samples made from commercial powders. The study of the microstructure formed during sintering of a number of oxides (partially stabilized ZrO_2 , Al_2O_3 with ZrO_2 , transparent materials based on Y_2O_3) shows that the most likely sintering mechanism is slippage of particles followed by self-consistent adjustment of the boundaries accompanying particle deformation as result of diffusion. So-called hot “self-pressing” is possible for small aggregates of the initial powder from which the article is fabricated. This phenomenon is due to surface tension forces acting in a porous article, which for particles a fraction of a micron in size reach several megapascals. This is why the sintering temperature decreases.

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